

# Generation, Spectroscopic Characterization, and Reactions of 3,4-Benzotropone. Distinctive Photochemical Behavior of 6,7-Benzobicyclo[3.2.0]hepta-3,6-dien-2-one in Rigid Glass at Low Temperature and in Fluid Solution

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**Abstract:** Irradiation of 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one (**2**) in a rigid glass at  $-196\text{ }^{\circ}\text{C}$  leads to the formation of 3,4-benzotropone (**1**), which exhibits a characteristic UV–vis absorption extending to 535 nm and dimerizes to give syn- and anti- $[\pi 8 + \pi 10]$  dimers **7** and **8** upon thawing the glass. The rate constant of the thermal dimerization of **1** is  $12 \pm 3\text{ M}^{-1}\text{ s}^{-1}$  at  $-78\text{ }^{\circ}\text{C}$ . Photochemically, **1** is stable under matrix isolation, but undergoes  $[\pi 10 + \pi 10]$  dimerization in solution. Compound **1** in a  $\text{CFCl}_3\text{--CF}_2\text{BrCF}_2\text{Br--CHCl}_3$  glass at  $-155\text{ }^{\circ}\text{C}$  shows an IR band at  $1506\text{ cm}^{-1}$  which is assigned to a vibration primarily involving C=O stretching mode by comparing the spectrum with that of  $^{18}\text{O}$ -labeled **1**. Under the same conditions tropone exhibits a C=O vibrational band at a significantly higher frequency ( $1553\text{ cm}^{-1}$ ), suggesting that the 3,4-benzo annulation makes the tropone ring more strongly polarized. The large contribution of a polar resonance form **1b** is reflected in the high affinity of **1** for protonation: **1** is nearly half-protonated in a 0.1 M solution of  $\text{CHCl}_2\text{CO}_2\text{H}$  in EPA (a 5:5:2 mixture of ether, isopentane, and ethanol). Furthermore, the electronic absorption spectrum undergoes a characteristic blue shift when the medium is changed from hydrocarbons to alcohols, suggesting that **1** is more polarized in the ground state than in the excited state. The generation of **1** from **2** is thermally effected also and, upon heating a mixture of **2** and olefin such as maleic anhydride or ethyl vinyl ether in benzene at  $220\text{ }^{\circ}\text{C}$ , adducts of the latter to **1** are obtained. The photochemical behavior of **2** is dependent on the state of medium in which **2** is irradiated; the photolysis of **2** in rigid glass results almost exclusively in the valence isomerization providing **1**, while in fluid solution predominantly in the di- $\pi$ -methane rearrangement affording 3,4-benzotricyclo[3.2.0.0<sup>2,7</sup>]hept-3-en-6-one (**19**). Plausible causes of the medium-dependent photochemical behavior of **2** are discussed.

## Introduction

3,4-Benzotropone (**1**) in which the benzo component is fused to the tropone ring in a manner to form a *o*-quinoidal structure has long been a subject of theoretical interest.<sup>1</sup> Ten  $\pi$ -electron peripheral conjugation is expected to give substantial aromatic character to **1** and to modify the reactivity of the *o*-quinodimethane system. Despite extensive exploration of the chemistries of troponoid<sup>2</sup> and *o*-quinoid<sup>3</sup> compounds, however, experimental information on *o*-quinoidal 3,4-benzotropones is surprisingly scarce and only a few derivatives have been reported so far, viz., the photochemical generation of 7-phenoxy-3,4-benzotropone **3**<sup>4</sup> by Chapman and the chemical trapping of dibenzotropones **4**<sup>5</sup> and **5**<sup>6</sup> by Bauld. The limited information led us to investigate the chemistry of parent compound **1** to gain

more detailed understanding on this system. By analogy with the known reactivity of benzocyclobutenes to isomerize to *o*-quinodimethanes,<sup>3,7</sup> we envisaged 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one (**2**) as a potential precursor of **1** and found that the electrocyclic ring-opening reaction of **2**, in fact, allowed the first generation and spectroscopic characterization of this elusive molecule.<sup>8</sup> In this paper, we describe details of the spectral and chemical properties of **1** which reveal significant electronic polarization in its ground state, viz., a substantial contribution of polar resonance form **1b** to the molecule. In the course of this study, moreover, photochemical behavior of **2** was found to depend on the state of the medium in which **2** is irradiated. Thus, the composition of photolysis products in rigid glass was markedly different from that in solution. These unexpected observations are also discussed here.

## Results and Discussion

**Preparation of 2.** Compound **2** was prepared by the addition of benzyne to 2-cyclopentenone acetal followed by hydrolysis and subsequent dehydrogenation of the resultant ketone **6** with DDQ.<sup>9</sup> Although the yield of the benzyne adduct was disap-

(1) Semiempirical SCF MO calculations predict that **1** has a bond-alternating structure and is only weakly stabilized (3.4 kcal/mol) by  $\pi$ -electron delocalization: (a) Kasinc, L.; Majerski, Z.; Trinajstić, N. *Z. Naturforsch., Teil A* **1968**, *23*, 192. (b) Dewar, M. J. S.; Trinajstić, N. *Croat. Chem. Acta* **1970**, *42*, 1. (c) Zambelli, N.; Trinajstić, N. *Z. Naturforsch., Teil B* **1971**, *26*, 1007.

(2) (a) Bergman, E. W. *Chem. Rev.* **1968**, *68*, 41. (b) Pietra, F. *Chem. Rev.* **1973**, *73*, 293.

(3) (a) Oppolzer, W. *Synthesis* **1978**, 793. (b) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270. (c) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873.

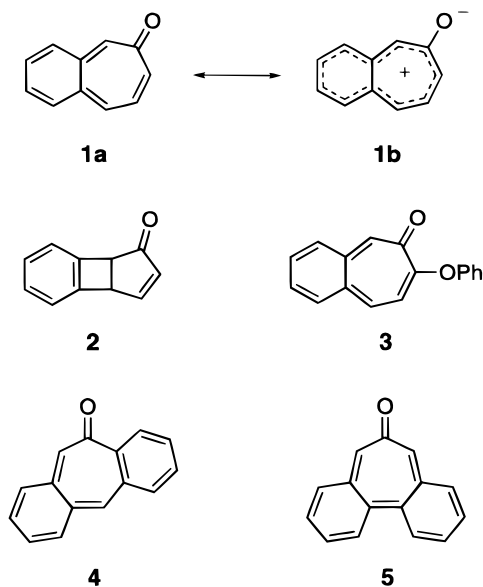
(4) (a) Chapman, O. L.; Smith, H. G.; King, R. W.; Pasto, D. J.; Stoner, M. R. *J. Am. Chem. Soc.* **1963**, *85*, 2031. (b) Chapman, O. L.; Busman, S. C.; Trueblood, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 7067.

(5) Bauld, N. L.; Rim, Y. S. *J. Am. Chem. Soc.* **1967**, *89*, 178.

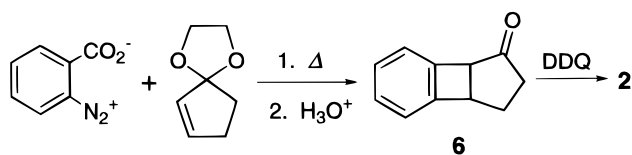
(6) Hudson, C. E.; Bauld, N. L. *J. Am. Chem. Soc.* **1973**, *95*, 3822.

(7) (a) Kolc, J.; Michl, J. *J. Am. Chem. Soc.* **1970**, *92*, 4147. (b) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280.

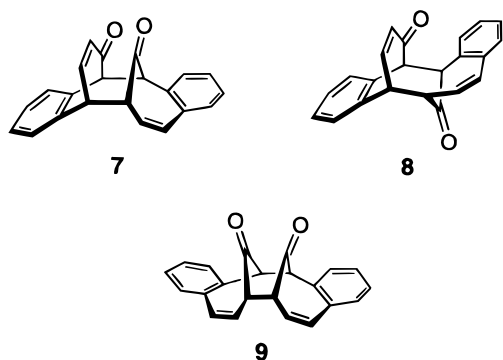
(8) For a preliminary account of a portion of this work, see: Ohkita, M.; Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1989**, 924.



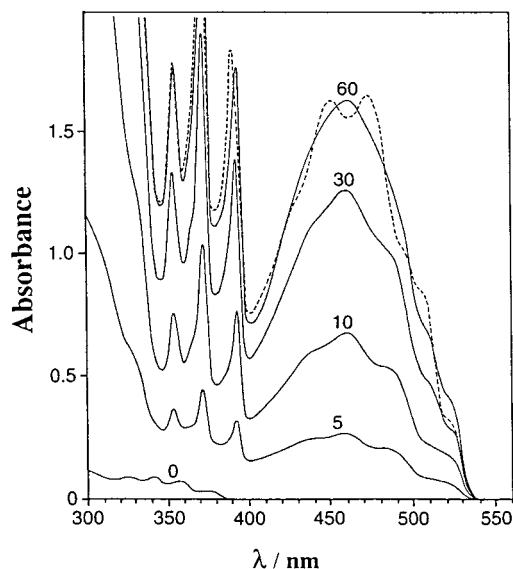
pointingly low, this preparation route was most straightforward. Acetalization of **2** followed by hydrolysis of the resultant acetal with  $\text{H}_2^{18}\text{O}$  gave  $^{18}\text{O}$ -labeled **2**<sup>10</sup>.



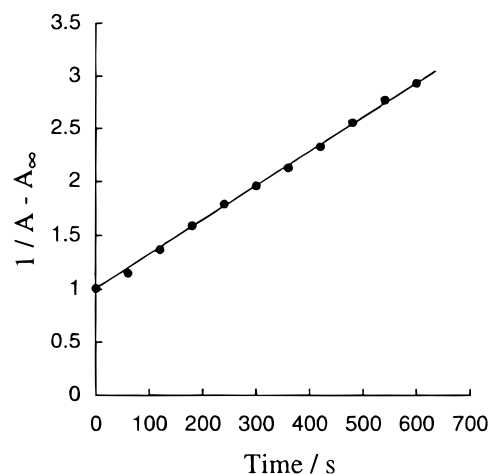
**Photochemical Generation of 1 from 2 in Rigid Glass at Low Temperature and Its Thermal and Photochemical Reactivities.** Since *o*-quinoidal (**1**) was expected to be a highly reactive, kinetically unstable molecule, the photochemical generation of **1** from **2** was first examined under matrix isolation at low temperature. When a degassed EPA (a 5:5:2 mixture of ether, isopentane, and ethanol) solution of **2** in a Pyrex tube was irradiated with a high-pressure mercury lamp at liquid nitrogen temperature ( $-196\text{ }^\circ\text{C}$ ), development of an intense absorption with fine structure was observed in the range 300–550 nm (Figure 1). The generated orange species was stable in the frozen EPA glass or in the fluid EPA solution below  $-130\text{ }^\circ\text{C}$ , but was consumed rapidly at  $-78\text{ }^\circ\text{C}$ . The decay of the absorption followed second-order kinetics, as shown in Figure 2, and, from the resultant photolyzate, two [ $\pi 8 + \pi 10$ ] dimers **7** and **8** were isolated in almost equal amounts in a combined yield of 80% (vide infra). Thus, we concluded that the photolysis



of **2** in EPA at  $-196\text{ }^\circ\text{C}$  led to the practically quantitative formation of **1** and that the observed spectrum was due to **1**. The rate constant for the dimerization of **1** is  $12 \pm 3\text{ M}^{-1}\text{ s}^{-1}$



**Figure 1.** Absorption spectral changes observed upon irradiation of **2** in an EPA glass at  $-196\text{ }^\circ\text{C}$  with a 500 W high-pressure mercury lamp through Pyrex (solid lines; numerals by the absorption curves indicate irradiation times in minutes) and further irradiation with a 500 W halogen lamp through a benzene solution of 9,10-dimethylantracene ( $>420\text{ nm}$ ) for 6 h (dashed line).

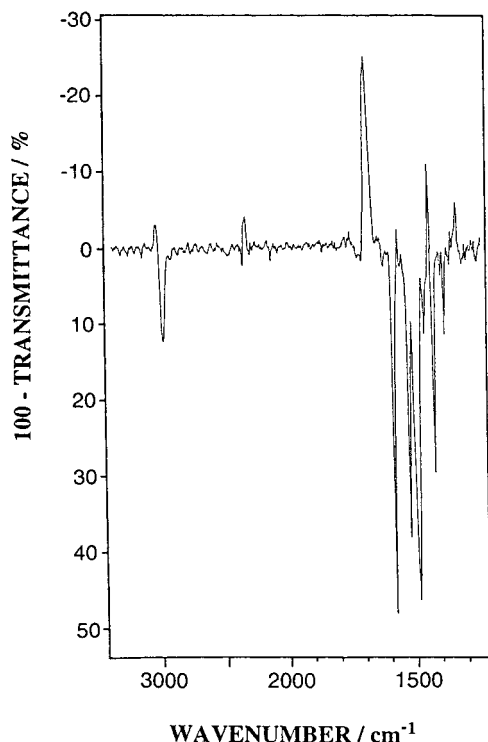


**Figure 2.** A plot of the reciprocal of absorbance vs time for the decay of the absorption at 458 nm in EPA at  $-78\text{ }^\circ\text{C}$ .

in EPA at  $-78\text{ }^\circ\text{C}$ . The molar absorptivity of **1** at  $\lambda_{\text{max}} = 458\text{ nm}$  in EPA was estimated to be about 2500 by assuming the quantitative formation of **1**. The development of absorption ascribable to **1** was also observed upon irradiation of **2** in an ethanol or methylcyclohexane/isopentane (4:1) glass at 77 K. The kinetic stability of **1** appeared to deteriorate in a hydrocarbon solvent, where **1** immediately disappeared upon thawing the glass below  $-100\text{ }^\circ\text{C}$ . The structural assignment of the dimers and their differentiation from each other were made on the basis of their spectroscopic data. Thus, the olefinic protons in the styryl moiety of **6** and those in the enone moiety of **8** resonate at distinctly higher field than the corresponding protons in the other isomer, due to shielding effects by the juxtaposed aromatic ring and styryl group, respectively. The above structural assignment was also supported by inspecting the magnitude of

(9) Compound **2** has previously been obtained via an independent route: Ohkita, M.; Tsuji, T.; Suzuki, M.; Murakami, M.; Nishida, S. *J. Org. Chem.* **1990**, *55*, 1506.

(10) For the preparation and IR spectrum of  $^{18}\text{O}$ -labeled tropone, see: (a) Krebs, A.; Schrader, B. *Liebigs Ann. Chem.* **1967**, *709*, 46. (b) Junge, H. *Spectrochim. Acta* **1968**, *24A*, 1951.



**Figure 3.** Difference IR spectrum (irradiated minus nonirradiated mixture) obtained by irradiating **2** with a high-pressure Hg lamp through Pyrex in  $\text{CFCl}_3\text{-CF}_2\text{BrCF}_2\text{Br-CHCl}_3$  (25:25:4) at  $-155^\circ\text{C}$ .

coupling constants between the vicinal bridgehead protons in those dimers.

Compound **1** is photochemically stable in the EPA glass at  $-196^\circ\text{C}$  and shows no tendency to undergo any unimolecular rearrangement. Thus, prolonged irradiation of **1** with long-wavelength light ( $>420\text{ nm}$ ) caused only minor changes in the shape of fine structure in its UV-vis absorption spectrum, presumably resulting from matrix relaxation. On the other hand, irradiation ( $>420\text{ nm}$ ) of **1** in a fluid EPA solution below  $-100^\circ\text{C}$  led to its smooth  $[\pi10 + \pi10]$  dimerization to give **9**. It has been reported that **3** also dimerizes thermally in a  $[\pi8 + \pi10]$  fashion, but it does so at a much slower rate ( $7.5\text{ M}^{-1}\text{ s}^{-1}$  at  $24^\circ\text{C}$  in ethanol).<sup>4b</sup> The 7-phenoxy substituent therefore lends substantially enhanced kinetic stability to **1**. It is interesting to note that, in contrast to **1**, **3** has been reported to give a single  $[\pi8 + \pi10]$  dimer corresponding to **7** and to undergo slow photolysis in an argon matrix to furnish 2-phenoxy-naphthalene and carbon monoxide presumably via the corresponding cyclopropanone valence isomer.<sup>4b</sup>

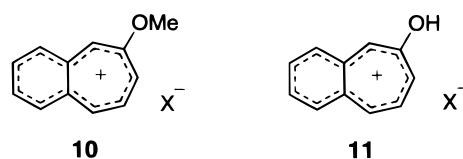
**Observation of 1 by IR Spectroscopy.** One of the major interests in **1** is the extent of electronic polarization, viz., that of the contribution of canonical form **1b**. The frequency of C=O vibrational band in IR spectrum is quite sensitive to substituent effects, and the measurement of IR spectrum of **1** is expected to provide a valuable insight into the electronic state of **1**. Tropone is a highly polarized species with substantial aromatic character, and the pronounced polarization of its C=O bond is reflected in an unusually low carbonyl frequency.<sup>10</sup>

Compound **2** exhibits a carbonyl absorption at  $1688\text{ cm}^{-1}$  in a  $\text{CFCl}_3\text{-CF}_2\text{BrCF}_2\text{Br-CHCl}_3$  (25:25:4) glass at  $-155^\circ\text{C}$ . Irradiation of the glass ( $>300\text{ nm}$ ) led to development of new absorption bands at 1594, 1538, 1506, and  $1438\text{ cm}^{-1}$  at the expense of the above absorption (Figure 3). When starting **2** was labeled with  $^{18}\text{O}$ , those bands were shifted to 1592, 1536,

1492, and  $1434\text{ cm}^{-1}$ , respectively. Therefore, the relatively broad third band at  $1506\text{ cm}^{-1}$  may be assigned to a vibration involving primarily C=O stretching mode while the other three bands may be assigned to those of principally C=C stretching character. Tropone exhibits a C=O vibrational band at  $1553\text{ cm}^{-1}$  under the same conditions. The unusually low C=O stretching frequency observed in **1** is noteworthy. The extent of isotope shift in the third band ( $14\text{ cm}^{-1}$ ), however, is only less than half of that expected for an uncoupled C=O vibration, suggesting the extensive mechanical coupling of the C=O stretching with the ring vibrations. Concomitant small shifts of the other three bands to lower frequencies are in line with the above inference. Thus, the results of the IR study appear to signify the large contribution of **1b** in the ground state, but it will be premature to derive the extent of electronic polarization in **1** from those results.<sup>10b,11</sup>

**Protonation of 1.** In accord with the results of IR measurement suggesting the significant electronic polarization in **1**, its electronic absorption spectrum was markedly dependent on the polarity of glass medium. Thus, when the medium was changed from methylcyclohexane-isopentane (4:1) to ethanol, the longest wavelength band was blue-shifted by ca. 15 nm, while the fine structure of the band was sharpened.<sup>12</sup> Moreover, a similar change in the absorption spectrum of **1** was observed when an EPA glass containing freshly generated **1** was thawed below  $-130^\circ\text{C}$  and refrozen at  $-196^\circ\text{C}$ . The observed changes in the electronic spectrum of **1** seem to be most reasonably accounted for by assuming the reorganization of solvent molecules including hydrogen bonding around highly polarized **1** upon thawing and refreezing the solution.

If the resonance form **1b** is a major contributor to the structure of **1**, then it should be a basic species. Compound **1** is indeed very readily protonated. Thus, the spectrum recorded after successively irradiating **2** in a 0.1 M solution of  $\text{CCl}_3\text{CO}_2\text{H}$  or  $\text{CF}_3\text{COOH}$  in EPA at  $-196^\circ\text{C}$ , thawing the mixture below  $-130^\circ\text{C}$ , and refreezing it at  $-196^\circ\text{C}$  was quite similar to that reported for the corresponding methoxybenzotropylium ion **10**,<sup>13</sup> demonstrating almost complete protonation of **1** in such a weakly acidic solution to generate **11** (Figure 4, spectrum A).

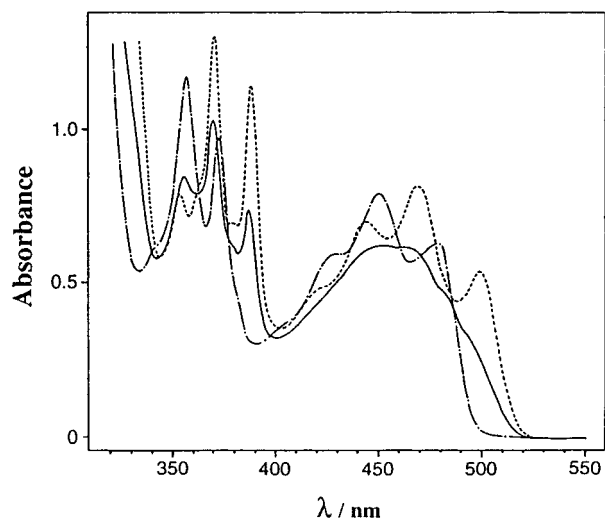


The initial spectrum before the thaw, however, was virtually superimposable to that in the absence of acid, showing that **1** remained unprotonated unless the glass was thawed. With less acidic  $\text{CH}_2\text{ClCO}_2\text{H}$ , on the other hand, **1** was not protonated and the spectrum recorded after refreezing the glass was essentially identical with that observed in the absence of acid (Figure 4, spectrum C). In a 0.1 M EPA solution of  $\text{CHCl}_2\text{-COOH}$ , **1** was nearly half-protonated to exhibit a spectrum corresponding to the superposition of the spectra of **1** and **11**

(11) (a) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen: London, 1958. (b) Bellamy, L. J. *Advances in Infrared Group Frequencies*; Methuen: London, 1968.

(12) Compound **1** shows  $\lambda_{\text{max}}$  at 355, 374, 395, 420, 442, 463, 488, and 523 nm in methylcyclohexane/isopentane (4:1) and at 352, 370, 388, 430 (sh), 447, 470, and 492 nm in ethanol. The bathochromic shifts of the absorption bands in the less polar former solvent suggest that **1** may be less polarized in the excited state than in the ground state: Bayliss, N. S.; McRae, E. G. *J. Phys. Chem.* **1954**, *58*, 1002.

(13) Simon, W.; Heilbronner, E.; Eschenmoser, A. *Helv. Chim. Acta* **1957**, *40*, 957.

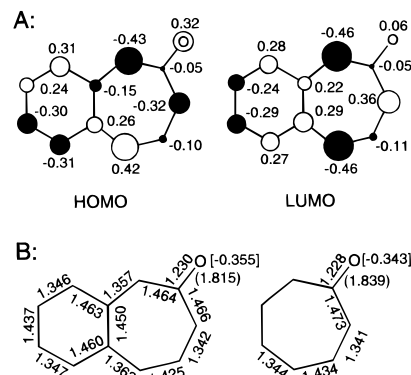
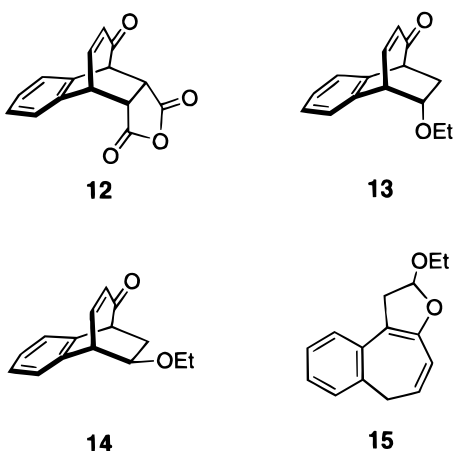


**Figure 4.** Absorption spectra observed after irradiating **2** in 0.1 M glassy EPA solutions of acids at  $-196\text{ }^{\circ}\text{C}$  with a high-pressure mercury lamp through Pyrex, thawing the resultant mixtures below  $-130\text{ }^{\circ}\text{C}$ , and refreezing them at  $-196\text{ }^{\circ}\text{C}$ : (A)  $\text{CCl}_3\text{CO}_2\text{H}$  (---), B:  $\text{CHCl}_2\text{-CO}_2\text{H}$  (—), C:  $\text{CH}_2\text{ClCO}_2\text{H}$  (---).

in a ratio of ca. 1:1 (Figure 4, spectrum B).<sup>14</sup> In the corresponding ethanolic solution, the extent of protonation was increased to ca. 80%.

It is of considerable interest to compare the basicity of **1** with that of tropone. A  $\text{p}K_{\text{a}}$  value of  $-1.02$  has been reported for the conjugate acid of tropone in water.<sup>15</sup> Unfortunately, the basicity of **1** could not be measured in water owing to its thermal instability. In contrast to **1**, however, tropone remains unprotonated in a 0.1 M ethanolic solution of  $\text{CF}_3\text{CO}_2\text{H}$ , indicating that tropone is substantially less basic, and hence electronically less polarized, than **1**.

**Thermal Generation of 1 from 2 and Its Trapping with Olefins.** The generation of **1** from **2** was thermally effected also. Thus, upon heating a mixture of **2** and 10 equiv of maleic anhydride in benzene at  $220\text{ }^{\circ}\text{C}$ , a single product was isolated in 52% yield and characterized as a  $[\pi 2 + \pi 8]$  adduct **12**. Below  $200\text{ }^{\circ}\text{C}$ , compound **2** remained virtually intact. When the thermolysis of **2** was carried out in the presence of ethyl vinyl ether, three volatile products were obtained in GLC yields of 10, 7, and 15%, respectively. The first and second products were assigned to the  $[\pi 2 + \pi 8]$  adducts, **13** and **14**, respectively, whereas the third product was assigned to the  $[\pi 2 + \pi 12]$  cycloaddition/1,5-hydrogen migration product **15** on the basis of their spectroscopic properties. Thermal cycloaddition reaction



**Figure 5.** (A) Coefficients of the frontier orbitals of **1** (PM3). (B) PM3-optimized bond lengths, bond orders (in parentheses), and atomic charges (in square brackets) in **1** and tropone.

of tropone has been extensively studied to reveal various reaction modes, depending on the properties of reacting olefins.<sup>3,16</sup> Electron-deficient dienophiles, for example, react with tropone in a  $[\pi 2 + \pi 4]$  manner whereas electron-rich olefins add in both  $[\pi 2 + \pi 4]$  and  $[\pi 2 + \pi 8]$  manner. Certain  $[\pi 2 + \pi 8]$  adducts of olefins to tropone undergo 1,5-hydrogen migration to yield thermodynamically more stable dihydrofurans as in the formation of **15**.<sup>16</sup> Thus, the modes of cycloaddition observed for **1** are closely similar to those for tropone.

**Computational Analysis.** In Figure 5 are summarized the results of theoretical calculations on **1** by semiempirical MNDO-PM3 method, together with those for tropone for comparison.<sup>17</sup> Particularly interesting are the findings that the order of the carbon–oxygen bond of **1** is lower and that negative atomic charge on the carbonyl oxygen of **1** is higher than those of tropone, respectively. These results suggest that **1** is electronically polarized more extensively than tropone and are in good accord with the experimental observations described in the preceding sections. In Figure 5 are also shown the frontier molecular orbitals of **1**. Coefficients for them are consistent with the peri- and regioselectivities observed in the thermal as well as photochemical reactions of **1**. The coefficients on the six-membered ring of **1** are slightly smaller than those on the tropone ring, suggesting the relative deficiency of reactivity in the former.

**Photochemical Behavior of 2 in Fluid Solution at Ambient Temperature.** Extensive study on the photochemical behavior of bicyclo[3.2.0]hepta-3,6-dien-2-ones demonstrates that the ring system is particularly liable to undergo di- $\pi$ -methane type rearrangement.<sup>18</sup> The clean generation of 3,4-benzotropone **1** from **2** in the glassy medium at low temperature, therefore, is rather exceptional for a derivative of that ring system. Interestingly, photolysis of **2** in fluid solution at ambient temperature led to a significantly different result from that in the frozen medium and furnished a set of products which would be mainly derived through initial di- $\pi$ -methane rearrangement. Thus, when

(14) For acidity constants of carboxylic acids in organic solvents, see: (a) Calder, G. V.; Barton, T. J. *J. Chem. Educ.* **1971**, *48*, 338. (b) Chantooni, M. K., Jr.; Kolthoff, I. M. *Anal. Chem.* **1979**, *51*, 133.

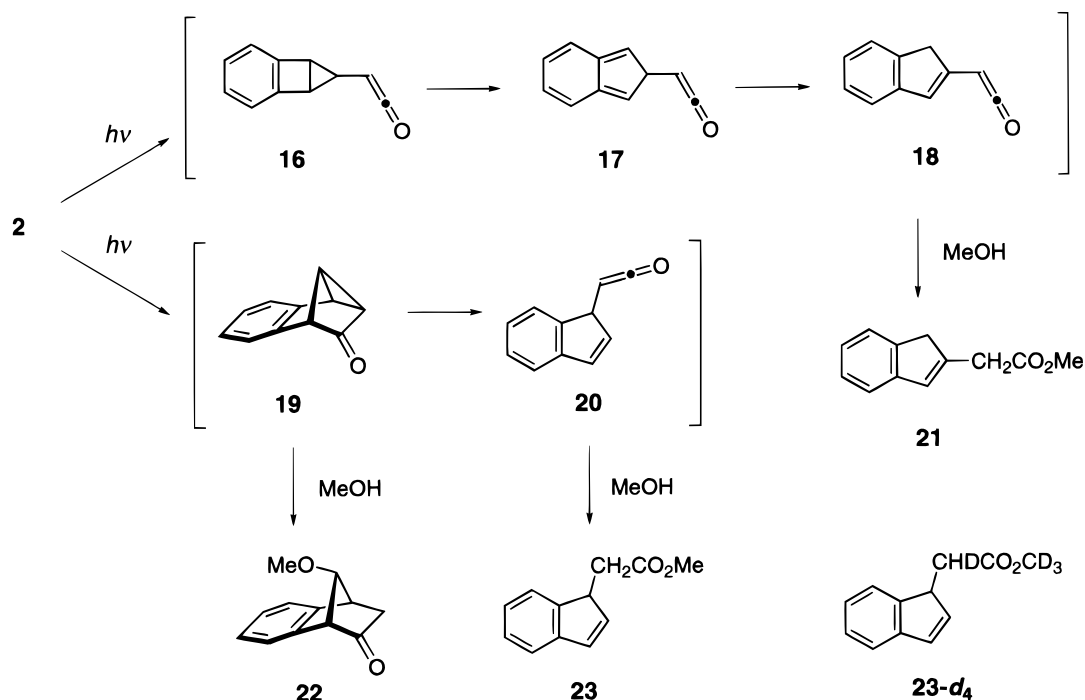
(15) (a) Hosoya, H.; Tanaka, J.; Nagakura, S. *Tetrahedron* **1962**, *18*, 859. (b) Hosoya, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1414.

(16) (a) Nozoe, T.; Mukai, T.; Nagase, T.; Toyooka, Y. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1247. (b) Oda, M.; Funamizu, M.; Kitahara, Y. *J. Chem. Soc., Chem. Commun.* **1969**, 737. (c) Cantrell, T. S. *Tetrahedron Lett.* **1975**, 907. (d) Cantrell, T. S. *J. Am. Chem. Soc.* **1971**, *93*, 2540.

(17) Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10. Hirano, T. *J. Chem. Phys.* **1989**, *91*, 36; Revised as Ver. 5.01 by Toyoda, J., for Apple Macintosh.

(18) (a) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (b) Schuster, D. I. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 17.

Scheme 1



a solution of **2** in methanol was irradiated with a high-pressure mercury lamp through Pyrex at 10 °C and the resulting photolyzate was stood for 2 days in the dark at room temperature, methanol adducts **21** (6.7%), **22** (8.9%), and **23** (34%) were formed along with small amounts of the dimers of **1** (**7** in 4.4%, **8** in 4.4%, and **9** in 3.6% yield). The adducts **22** and **23** gradually built up in the dark over the 2 days after the irradiation, indicating their formation via secondary thermal reactions from the primary photoproduct(s). Compound **22** was produced as a single stereoisomer in which the methoxy group was introduced anti to the carbonyl group, as confirmed by the absence of long-range coupling between H-7 and *endo*-H-3 in its  $^1\text{H}$  NMR spectrum.

The photochemical transformation of **2** into the methanol adducts **21–23** may be rationalized in terms of initial  $\alpha$ -cleavage and di- $\pi$ -methane rearrangement as outlined in Scheme 1. Thus, ring contraction in **2** via the  $\alpha$ -cleavage<sup>19</sup> produces cyclopropylketene **16** which subsequently undergoes successive valence isomerization<sup>20</sup> and methanol addition to give ester **21**. On the other hand, the di- $\pi$ -methane rearrangement<sup>21</sup> in the electronically excited **2** leads to the formation of 3,4-benzocyclo[3.2.0.0<sup>2,7</sup>]hept-3-en-6-one **19** from which **22** and **23** are produced via the secondary thermal reactions: homoconjugate addition<sup>22</sup> of methanol to **19** stereoselectively affords ether **22**, while ring cleavage<sup>21,22</sup> in **19** yields ketene **20** which is in turn captured by methanol to give ester **23**. Although **19** lacked

sufficient stability to be isolated in a pure form at room temperature, its intermediacy was confirmed by monitoring the reaction by IR and NMR spectroscopy. Thus, photolysis of **2** in  $\text{CHCl}_3$  at  $-10$  °C led to development of a  $\text{C}=\text{O}$  vibrational band at  $1749\text{ cm}^{-1}$  which was gradually replaced in the dark by a new band at  $2116\text{ cm}^{-1}$ , in accord with the initial formation of cyclobutanone **19** and its thermal conversion into ketene **20**. The  $^1\text{H}$  NMR spectrum recorded after irradiating **2** at  $-10$  °C in  $\text{CDCl}_3$ , moreover, indicated the formation of species exhibiting four aliphatic proton signals at  $\delta$  3.11, 3.33, 4.05, and 4.10 besides four aromatic proton signals at  $\delta$  7.1–7.4 in ca. 50% yield, to which structure **19** was reasonably assigned on the basis of the similarity of the spectrum to those of the related compounds (Figure 6).<sup>23</sup> When the resultant solution was diluted with  $\text{CD}_3\text{OD}$  and allowed to stand in the dark at room temperature, the above signals were mainly replaced by those of **23-d<sub>4</sub>**.

**Plausible Causes of the Medium-Dependent Photochemical Behavior of 2.** The most remarkable feature of the present photochemical reaction is dependence of the photochemical behavior of **2** on the state of reaction medium. By monitoring the reaction by IR, UV-vis, and  $^1\text{H}$  NMR spectroscopies, it was demonstrated that **2** preferentially undergoes the valence isomerization into **1** in rigid glassy medium at low temperature without noticeable complication by competing reactions, in contrast to the selective transformation into **19** in fluid solution at ambient temperature. The factor first to be considered for the divergent results will probably be the spin multiplicity of species responsible for the formation of **1**, **16**, and **19**. Since the energy of the lowest excited state ( $E_T$ ) of 2-cyclopentenone is 73–74 kcal/mol above the ground state,<sup>24,25</sup> we chose *trans*-

(19) Cyclopentenones bearing a radical stabilizing group at C-5 position undergo  $\alpha$ -cleavage to afford the corresponding cyclopropyl ketenes: Agosta, W. C.; Smith, A. B., III *J. Am. Chem. Soc.* **1971**, *93*, 5513.

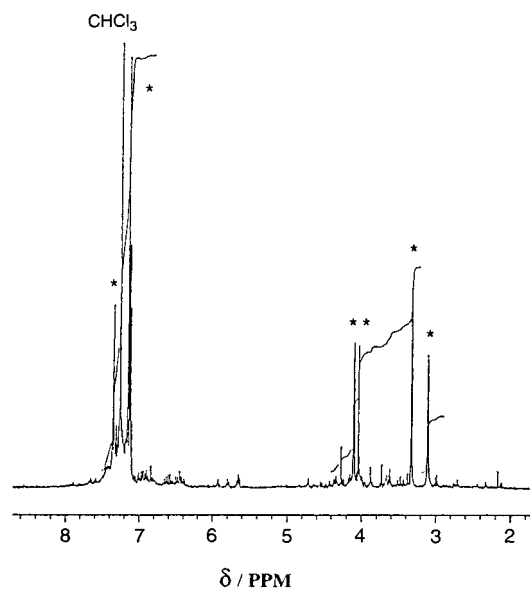
(20) An activation energy of  $18.9 \pm 0.2$  kcal/mol has been reported for the thermal rearrangement of 5,5-dimethylbenzobicyclo[2.1.0]pent-2-ene to 2,2-dimethylisoidene: Dolbier, W. R., Jr.; Matsui, K.; Dewey, H. J.; Horák, D. V.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 2136.

(21) Cyclopentenones bearing an aromatic ring at C-4 position undergo di- $\pi$ -methane rearrangement to yield substituted bicyclo[2.1.0]pentan-2-ones which subsequently undergo spontaneous cycloreversion to ketene derivatives at room temperature: Zimmermann, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623.

(22) (a) Gilbert, J. C.; Luo, T.; Patel, U. *J. Org. Chem.* **1981**, *46*, 4042. (b) Smith, A. B., III.; Toder, B. H.; Richmond, R. E.; Branca, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4001.

(23) (a) Adam, W.; Hill, K. *J. Am. Chem. Soc.* **1985**, *107*, 3686. (b) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4554. (c) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 7250.

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**Figure 6.** 500 MHz  $^1\text{H}$  NMR spectrum recorded after irradiating **2** in  $\text{CDCl}_3$  with 365 nm light at  $-10^\circ\text{C}$ . The signals marked with an asterisk were assigned to **19**.

**Table 1.** Quenching and Sensitization of Photolysis of **2**<sup>a</sup>

additive	conc (M)	relative conv <sup>b,c</sup>	relative yields <sup>b</sup>			dimers of <b>1</b>
			<b>21</b>	<b>22</b>	<b>23</b>	
piperylene <sup>d</sup>	1.0	0.37	0.17	$\leq 0.20$	0.38	$\leq 0.10$
xanthone <sup>e</sup>	$1.2 \times 10^{-2}$	1.20	1.21	1.60	0.64	1.20

<sup>a</sup> Deaerated  $2.0 \times 10^{-2}$  M solutions of **2** in methanol were irradiated with light of  $\lambda = 313$  nm for 30 min and then allowed to stand for 2 days in the dark at room temperature before analyzing the resultant mixtures by GC and HPLC using dimethyl phthalate as an internal standard. <sup>b</sup> Relative to the values in the absence of the additives. <sup>c</sup> The conversion of **2** was 35% in the absence of the additives. <sup>d</sup> The absorption of incident light by the quencher was negligible. <sup>e</sup> More than 95% of incident light was absorbed by the sensitizer.

piperylene ( $E_T = 58.8$  kcal/mol) as a triplet quencher and xanthone ( $E_T = 74.2$  kcal/mol) as a triplet sensitizer.<sup>26</sup> As summarized in Table 1, all the productions of the dimers of **1**, **21**, **22**, and **23** were suppressed in the presence of the former, whereas they were facilitated in the presence of the latter, indicating the derivation of all the products from the triplet excited state of **2**. Accordingly, the differentiation in the product compositions in the different media is not attributable to difference in the spin multiplicity of species involved in the transformations of **2** into **1** and into **16** and **19**. Another possibility by which the divergent results are apparently explained is the facile transformation of **1** into **16** and **19** by a secondary thermal or photochemical process, possibly via the cycloreversion to **2**, in fluid solution at ambient temperature. However, the composition of photolyzate of **2** in methanol, more specifically the ratio  $(7 + 8)/(21 + 22 + 23)$ , remained virtually unchanged in the temperature range  $+80$  to  $-80^\circ\text{C}$  (Table 2) and irradiation of **1** in fluid EPA at  $-100^\circ\text{C}$  led almost exclusively to the formation of **9** as previously described. This observation may also allow to rule out, though not rigorously, the possibility that a much smaller Arrhenius factor for the formation of **1** than for the isomerization to **16** and **19** gives rise to the different photochemical behavior of **2** under the different conditions.

(25) Loutfy, R. O.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1970**, 1040.

(26) Cowan, D. O.; Drisko, R. D. *Elements of Organic Photochemistry*; Plenum: New York, 1979, Chapter 5.

**Table 2.** Product Distributions in Photolysis of **2** in Methanol at Different Temperatures<sup>a</sup>

temp ( $^\circ\text{C}$ )	state	conv (%)	yields (%)			
			<b>21</b> <sup>b</sup>	<b>22</b> <sup>b</sup>	<b>23</b> <sup>b</sup>	dimers of <b>1</b> <sup>c</sup>
80	fluid	65	9	2	34	15
10	fluid	55	8	8	36	15
$-80$	fluid	36	8	8	37	10
$-196$	solid	8	0	0.3	3	60

<sup>a</sup> Deaerated methanolic solutions of **2** in Pyrex ampules were irradiated with a high-pressure mercury lamp at the specified temperatures and allowed to stand in the dark for 2 days at room temperature before analyzing the resultant mixtures. <sup>b</sup> Determined by GLC. <sup>c</sup> Determined by HPLC.

It has been known that the ring-opening reactions of certain polycyclic cyclobutenes proceed by a two-photon mechanism via their triplet excited states, specifically in rigid, low-temperature medium.<sup>27</sup> Neither the measurement of photolysis rate of **2** as a function of light intensity nor a double beam experiment, however, supported the operation of that mechanism in the transformation of **2** into **1**. Thus, the rate of generation of **1** in rigid EPA glass at 77 K was only linearly proportional to the intensity of irradiated light (365 nm) and remained unperturbed by simultaneous irradiation of the glass with long-wavelength light ( $>415$  nm) using a xenon lamp.

The results of quenching/sensitization experiments suggest that the intrinsic reactivity of **2** in the triplet excited state is reflected in the product composition in fluid medium and that, of the available reaction pathways, the channels leading to the formation of **16** and **19** are somehow hindered in rigid media to allow the intrinsically less favored valence isomerization into **1** to predominate the reaction. A characteristic feature of constraining rigid medium is restriction on a change of molecular shape by the wall of cavity in which the molecule resides.<sup>28</sup> There are many examples which demonstrate that constraining media such as crystals<sup>29,30</sup> and polymers<sup>31</sup> influence the abilities of guest molecules to change their shapes during the course of photoreactions. This concept of steric constraint on the changes of molecular shapes in organized media may be extended to photochemical reactions in rigid glasses.<sup>32</sup> The isomerization of **2** to **16** and **19** seems to proceed stepwise by way of triplet biradicals **24** and **25/26**, respectively, which, after intersystem crossing to the corresponding singlet species, collapse to afford **16** and **19** or revert to **2** (Scheme 2). The suppression of formation of **16** and **19** in the glassy medium at low temperature might result from the inadequate space of rigid cavity to accommodate the shape changes that accompany the generation of the biradical intermediates or their subsequent transformations. The degree of shape change that occurs as **2** is transformed into **1** seems to be relatively minor as compared with those in the rearrangement of **2** into **16** and **19**. According to the

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(28) Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, 26, 530 and references therein.

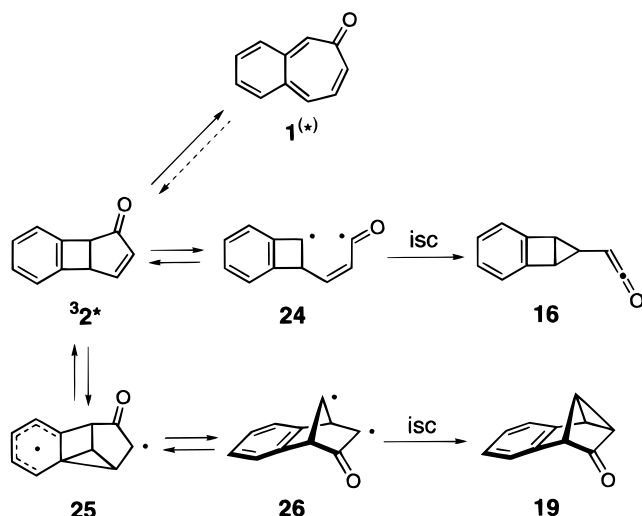
(29) Zimmerman, H. E.; Zhu, Z. *J. Am. Chem. Soc.* **1995**, 117, 5245 and references therein.

(30) Irradiation of microcrystalline **2** in a KBr pellet resulted in the [2 + 2] photodimerization.

(31) (a) Gudmundsdottir, A.; Scheffer, J. R. *Tetrahedron Lett.* **1989**, 30, 419, 423. (b) Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J.; Yap, M. *J. Org. Chem.* **1992**, 57, 1486.

(32) (a) Loutfy, R. O.; Yates, P. *J. Am. Chem. Soc.* **1979**, 101, 4694. (b) Yabe, A. *Bull. Chem. Soc. Jpn.* **1980**, 53, 2933. (c) Tomioka, H.; Watanabe, T.; Hirai, K.; Furukawa, K.; Takui, T.; Itoh, K. *J. Am. Chem. Soc.* **1995**, 117, 6376.

## Scheme 2



semiempirical calculations, the sum of non-hydrogen atom displacements in proceeding from **2** to **1** (0.506 Å/atom) is slightly smaller than that to **19** (0.551 Å/atom).<sup>33,34</sup> Due to the more extended conjugation in **1** than in **2**, moreover, the excited triplet state energy of the product **1** is expected to be significantly lower than that of the reactant **2**. In such an energetic situation, photochemical transformation may well proceed adiabatically, especially in triplet excited states, directly delivering products in their electronically excited states.<sup>35,36</sup> The adiabatic conversion of **2\*** into **1\*** might be significantly less susceptible to the steric constraint imposed by the rigid media than the stepwise isomerization of **2\*** to **16** and **19**, and might preferentially, practically irreversibly proceed in the organic glasses at low temperature.

## Conclusions

The photochemical isomerization of **2** under matrix isolation at low temperature allowed the generation and spectroscopic characterization of parent 3,4-benzotropone (**1**). The spectroscopic study reveals that **1** is significantly polarized in the ground state, in accord with theoretical calculations. Such highly polarized compounds have recently attracted considerable attention in the field of optical materials. Suitable structural modification of **1** may lead to the development of the stable derivatives of unique optical properties. Unexpectedly, **2** exhibits medium-dependent photochemical behavior; while the isomerization to **1** selectively occurs in rigid glass, the rearrangements to afford **16** and **19** as intermediates are preferred in fluid solution. Although the reason for the divergent photochemical behavior of **2** is not fully understood, mechanistic investigation suggests that the latter processes might sterically be impeded in the constraining rigid glassy medium.

## Experimental Section

<sup>1</sup>H and <sup>13</sup>C NMR were recorded with JEOL FX-100 and FX-500 spectrometers in CDCl<sub>3</sub> in the High-Resolution NMR Laboratory at Hokkaido University. IR spectra were taken on Hitachi Model 270-30

(33) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974.

(34) Overlay analysis (minimization of sum of non-hydrogen atom displacements) was performed on the molecular modeling system *CS Chem 3D Pro V. 3.5* (CambridgeSoft Corp.; Cambridge, MA) using the PM3 optimized geometries.

(35) For a review, see: Turro, N. J.; McVey, J.; Ramamurthy, V.; Lechtken, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 572.

(36) For the adiabatic electrocyclic ring-opening of cyclobutenes in their singlet excited states, see: Leigh, W. J.; Postigo, J. A.; Venneri, P. C. *J. Am. Chem. Soc.* **1995**, *117*, 7826 and references therein.

grating spectrometer. Mass spectra were recorded on JEOL Model DX303 spectrometer at an ionization voltage of 70 eV. UV spectra were taken on a Cary Model 17 spectrometer. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University. GLC work was done on Hitachi 063 and 163 gas chromatographs with helium as a carrier gas. HPLC analysis was conducted on a Hitachi Model 635 liquid chromatograph using a 3.9 mm × 30 cm column packed with  $\mu$ -Porasil. The light sources for photochemistry were a Halos (Eiko-sha, Japan) 450 W high-pressure Hg lamp and a Toshiba 500 W halogen lamp. Cyclopent-2-en-1-one acetal,<sup>37</sup> benzenediazonium-2-carboxylate,<sup>38</sup> and tropone<sup>39</sup> were prepared following the known procedures. Other reagents and solvents were obtained from commercial sources and purified prior to use.

**6,7-Benzobicyclo[3.2.0]hept-6-en-2-one (6).** A suspension of benzenediazonium-2-carboxylate,<sup>38</sup> prepared from 34.2 g of anthranilic acid (0.25 mol), and 90 g of cyclopent-2-en-1-one acetal (0.71 mol) in 400 mL of dioxane was heated at 50 °C until gas evolution ceased (for 5 h). The reaction mixture was cooled to room temperature, poured into 600 mL of 5% NaHCO<sub>3</sub>(aq), and extracted with hexane (5 × 300 mL). The extracts were combined, washed successively with 5% NaHCO<sub>3</sub>(aq), water, and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. After the solvent and unreacted cyclopent-2-en-1-one acetal were evaporated, the residue was dissolved in 60 mL of 50% AcOH(aq) and heated at 50 °C for 4 h. The reaction mixture was poured into 100 mL of water and the hydrolyzed product was extracted with ether (5 × 100 mL). The combined extracts were washed well with 5% NaHCO<sub>3</sub>(aq), dried with MgSO<sub>4</sub>, concentrated, and subjected to chromatography on silica gel eluted with ether/hexane (5:95) to afford crude **6**, which was further purified by distillation to give 1.6 g (4% from anthranilic acid) of **6** as a colorless liquid: bp 100–115 °C (bath temperature)/2 Torr; <sup>1</sup>H NMR  $\delta$  2.04–2.78 (m, 4 H), 3.88 (d, *J* = 3.8 Hz, 1 H), 4.12 (dd, *J* = 6.5 and 3.8 Hz, 1 H), 7.04–7.37 (m, 4 H); <sup>13</sup>C NMR  $\delta$  24.07, 34.72, 44.75, 54.38, 121.95, 122.36, 127.89, 128.32, 141.90, 147.63, 215.17; IR (film) 1740 cm<sup>-1</sup>; UV  $\lambda_{\text{max}}$  (EtOH) 265 ( $\epsilon$  1400, sh), 269 (1830), 275 (1900), 301 nm (540); MS *m/z* 158 (M<sup>+</sup>, 53), 130 (99), 129 (100). Anal. Calcd for C<sub>11</sub>H<sub>12</sub>O: C, 83.52; H, 6.37. Found: C, 83.45; H, 6.39.

**6,7-Benzobicyclo[3.2.0]hepta-3,6-dien-2-one (2).** A solution of 1.6 g of **23** (10 mmol) and 3.2 g of DDQ (14 mmol) in 40 mL of benzene was distributed among three glass ampules (20 mm i.d.). The ampules were sealed and heated at 150 °C for 32 h. The ampules were opened and the combined reaction mixture was diluted with 60 mL of benzene, washed successively with 5% NaHCO<sub>3</sub>(aq) and brine, and dried with MgSO<sub>4</sub>. After removal of the solvent, the residue was chromatographed on silica gel eluted with ether/hexane (3:7) to afford 0.73 g of **2** (46%). Compound **2** obtained above was identical in all respects with that obtained previously.<sup>9</sup>

**Preparation of <sup>18</sup>O-Labeled 2.** A mixture of 85 mg of **2** (0.51 mmol), 2 mL of ethylene glycol, and 45 mg of PPTS (0.18 mmol) in 15 mL of benzene was heated under reflux and the condensate was returned to the mixture through a column packed with molecular sieves 4A pellets to remove the water formed. After 21 h, the GLC analysis (5% PEG20M, 1 m, 150 °C) of the mixture showed complete consumption of **2**. The mixture was cooled to room temperature, diluted with ether, washed successively with saturated Na<sub>2</sub>CO<sub>3</sub>(aq) and brine, and dried with MgSO<sub>4</sub>. After removal of the solvent, the residue was chromatographed on silica gel eluted with ether/hexane (1:4) to give 27 mg of acetal **24** (26%): mp 85–87 °C; <sup>1</sup>H NMR  $\delta$  3.93 (d, *J* = 3.7 Hz, 1 H), 4.00–4.16 (m, 4 H), 4.44 (dd, *J* = 3.7 and 2.9 Hz, 1 H), 5.58 (d, *J* = 5.6 Hz, 1 H), 6.38 (dd, *J* = 5.6 and 2.9 Hz, 1 H), 7.02–7.25 (m, 4 H); IR (KBr) 1614 cm<sup>-1</sup>; MS *m/z* 200 (M<sup>+</sup>, 20), 128 (100); HRMS calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub> 200.0837, found 200.0831.

A mixture of 11 mg of **24** (0.055 mmol), 250 mg of H<sub>2</sub><sup>18</sup>O (12.5 mmol, 97% <sup>18</sup>O, Aldrich), and a catalytic amount of *p*-TsOH in 5 mL of dry THF was stirred at 40 °C. After 7 h, the mixture was cooled to room temperature, diluted with 40 mL of benzene, and washed with 20 mL of saturated Na<sub>2</sub>CO<sub>3</sub>(aq). The aqueous layer was extracted with

(37) Garbish, E. W., Jr., *J. Org. Chem.* **1965**, *30*, 2109.

(38) Logullo, F. M.; Seitz, A. H.; Friedman, L. *Org. Synth.* **1973**, Coll. Vol. 5, 54.

(39) (a) Doering, W. von E.; Sayigh, A. A. *J. Am. Chem. Soc.* **1954**, *76*, 6, (b) Jones, G. J. *Chem. Soc., C* **1970**, 1230.

30 mL of benzene, and the organic layer and the organic extracts were combined, washed successively with water and brine, and dried with  $\text{MgSO}_4$ . After removal of the solvent, the crude product was subjected to preparative GLC to give 4.3 mg of **2** [95%  $^{18}\text{O}$ ] (50%); MS  $m/z$  158 ( $\text{M}^+$ , 32.5) 128 (100).

**Measurement of the Electronic Absorption Spectra of 3,4-Benzotropone (1).** A solution of **2** in an appropriate solvent was placed in a Pyrex tube (12 mm i.d.) and degassed by freeze–thaw cycles. The sealed tube was immersed in liquid  $\text{N}_2$  in a Dewar having two parallel windows (22 mm diameter) facing each other and irradiated through the window.

When a solution of **2** ( $3.3 \times 10^{-4}$  M) in 7 mL of EPA was irradiated with a high-pressure Hg lamp at  $-196^\circ\text{C}$ , development of an absorption with  $\lambda_{\text{max}}$  at 353, 372, 392, 438 (sh), 458, 482 (sh), 506 (sh), and 518 (sh) nm was observed. Absorbances at 458 nm after 2, 5, 10, and 30 min of irradiation were 0.25, 0.46, 0.66, and 1.25, respectively, and it was increased upon further irradiation. The molar absorptivity of **1** at 458 nm in EPA was estimated to be 2500 by assuming the quantitative transformation of **2** to **1**. The conversion of **2** was determined by GLC analysis of the photolyzate. The absorption assigned to **1** remained unchanged for more than 1 h at  $-196^\circ\text{C}$ , but disappeared rapidly when the frozen solution was thawed in ethanol at  $-78^\circ\text{C}$ . The decay of the absorption followed second-order kinetics and the rate constant determined by monitoring the decay at 458 nm was  $12 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$  in EPA at  $-78^\circ\text{C}$ . When an EPA glass containing freshly generated **1** was thawed in slushy pentane below  $-130^\circ\text{C}$  and refrozen at  $-196^\circ\text{C}$ , the shape of absorption spectrum was altered into one with  $\lambda_{\text{max}}$  at 352, 368, 387, 423, 444, 471, and 500 nm. The latter spectrum was reproduced without loss of intensity when the thaw–refreeze cycle was repeated.

**Thermal [ $\pi 8 + \pi 10$ ] Dimerization of 1.** A solution of 50 mg of **2** (0.32 mmol) in 28 mL of EPA ( $1.1 \times 10^{-2}$  M) was distributed among four quartz ampules (12 mm i.d.) and degassed by freeze–pump–thaw cycles. The solution in each sealed ampule was frozen in liquid  $\text{N}_2$ , irradiated with a high-pressure Hg lamp through Pyrex for 1 h, and then warmed to room temperature. This freeze–irradiation–thaw cycle was repeated 10 times for each sample before the irradiation was discontinued. HPLC analysis ( $\mu$ -Porasil, ether/hexane 1:2) of the resultant photolyzate indicated the exclusive formation of **7** and **8** from **2**. When the photolyzate was allowed to stand at room temperature for 5 days, the dimer **8** separated from the solution as colorless crystals. After the crystals were collected (4 mg), the filtrate was evaporated and the residue was chromatographed on silica gel eluted with ether/hexane (1:9) to afford 20 mg of **2** (40% recovery). Further elution with ether/hexane (1:1) gave 20 mg of a mixture of the dimers (total 24 mg, 80% yield), which was subjected to fractional crystallization from 50 mL of ether to give 6 mg of pure **8**. After removal of the solvent from the filtrate, the residue (14 mg) was subjected again to chromatography on silica gel (Merck Lobar A column). Elution with ether/hexane (1:4) produced a 95:5 mixture of **7** and **8**, which was recrystallized from hexane to give 9 mg of pure **7**: mp  $>320^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  3.98 (ddd,  $J = 6.8, 5.9$  and  $2.5$  Hz, 1 H), 4.10 (dd,  $J = 9.3$  and  $5.9$  Hz, 1 H), 4.12 (dd,  $J = 4.9$  and  $1.5$  Hz, 1 H), 4.40 (dd,  $J = 4.9$  and  $2.5$  Hz, 1 H), 5.37 (dd,  $J = 12.2$  and  $6.8$  Hz, 1 H), 6.03 (d,  $J = 12.2$  Hz, 1 H), 6.11 (dd,  $J = 11.7$  and  $1.5$  Hz, 1 H), 6.65 (d,  $J = 7.3$  Hz, 1 H), 6.87 (d,  $J = 7.8$  Hz, 1 H), 6.96 (td,  $J = 7.3$  and  $1.5$  Hz, 1 H), 7.03 (d,  $J = 7.3$  Hz, 1 H), 7.11–7.15 (m, 2 H), 7.15 (dd,  $J = 11.7$  and  $9.3$  Hz, 1 H), 7.29 (td,  $J = 7.3$  and  $1.5$  Hz, 1 H), 7.32 (d,  $J = 7.8$  Hz, 1 H); IR (film) 1704,  $1662 \text{ cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) 261 ( $\epsilon$  11 000), 268 (10 000), 300 nm (1800, sh); MS  $m/z$  312 ( $\text{M}^+$ , 27), 128 (100); HRMS calcd for  $\text{C}_{22}\text{H}_{16}\text{O}_2$  312.1150, found 312.1158. **8**: mp  $248.5$ – $250^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  4.01 (ddd,  $J = 9.0, 7.3$  and  $2.2$  Hz, 1 H), 4.26 (dd,  $J = 9.3$  and  $9.0$  Hz, 1 H), 4.52 (dd,  $J = 10.7$  and  $1.2$  Hz, 1 H), 4.74 (dd,  $J = 10.7$  and  $2.2$  Hz, 1 H), 5.67 (dd,  $J = 11.7$  and  $1.2$  Hz, 1 H), 5.79 (dd,  $J = 11.9$  and  $7.3$  Hz, 1 H), 6.49 (d,  $J = 11.9$  Hz, 1 H), 6.91 (dd,  $J = 11.7$  and  $9.3$  Hz, 1 H), 7.10–7.31 (m, 8 H); IR (KBr) 1702,  $1664 \text{ cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) 258 ( $\epsilon$  10 000), 268 (9000), 300 nm (1300, sh); MS  $m/z$  312 ( $\text{M}^+$ , 21), 128 (100); HRMS calcd for  $\text{C}_{22}\text{H}_{16}\text{O}_2$  312.1150, found 312.1141.

**Photochemical [ $\pi 10 + \pi 10$ ] Dimerization of 1.** A solution of 9 mg of **2** in 200 mL of EPA was distributed among 30 Pyrex tubes (12

mm i.d.). The solution in each tube was irradiated with a high-pressure Hg lamp at  $-196^\circ\text{C}$ , whereupon absorbance at 458 nm went up to over 1.3. The frozen solution was thawed in an ethanol bath at  $-100^\circ\text{C}$  and irradiated immediately with a 500 W halogen lamp through a solution filter of 9,10-dimethylanthracene in benzene ( $>420$  nm light) at the same temperature. The orange coloration of the solution due to **1** was discharged within minutes. The photolyzed mixtures in the 30 tubes were combined, concentrated, and analyzed by HPLC ( $\mu$ -Porasil, ether/hexane 1:2), which showed the formation of **9** together with small amounts of **7** and **8**. The mixture was subjected to preparative HPLC to give 2 mg of **9**: mp  $218.5$ – $219.5^\circ\text{C}$ ;  $^1\text{H}$  NMR  $\delta$  3.68 (d,  $J = 5.4$  Hz, 2 H), 3.88 (s, 2 H), 5.66 (dd,  $J = 12.2$  and  $5.4$  Hz, 2 H), 6.00 (d,  $J = 12.2$  Hz, 2 H), 7.02 (dd,  $J = 7.3$  and  $1.5$  Hz, 2 H), 7.19 (dd,  $J = 7.3$  and  $1.5$  Hz, 2 H), 7.24 (td,  $J = 7.3$  and  $1.5$  Hz, 2 H), 7.27 (td,  $J = 7.3$  and  $1.5$  Hz, 2 H); IR (KBr) 1718,  $1632 \text{ cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (EtOH) 210 ( $\epsilon$  20 000, sh), 254 nm (12 600); MS  $m/z$  312 ( $\text{M}^+$ , 29), 128 (100); HRMS calcd for  $\text{C}_{22}\text{H}_{16}\text{O}_2$  312.1150, found 312.1121.

**Protonation of 1.** A solution of **2** ( $3.2 \times 10^{-4}$  M) in 7.5 mL of EPA containing an appropriate carboxylic acid (71 mg of  $\text{CH}_2\text{ClCO}_2\text{H}$ , 62 mg of  $\text{CHCl}_2\text{CO}_2\text{H}$ , or 122 mg of  $\text{CCl}_3\text{CO}_2\text{H}$ ) was placed in a quartz tube (12 mm i.d.) and degassed by freeze–pump–thaw cycles. The tube was sealed, immersed in liquid  $\text{N}_2$ , and irradiated with a high-pressure Hg lamp through Pyrex for 30 min. The resulting mixture was then thawed in slushy pentane below  $-130^\circ\text{C}$  and immediately refrozen at  $-196^\circ\text{C}$ , and a UV–vis absorption spectrum was recorded: UV–vis  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{ClCO}_2\text{H}/\text{EPA}$ ) 351, 367.5, 385.5, 442.5, 467, 497.5 nm;  $\lambda_{\text{max}}$  ( $\text{CHCl}_2\text{CO}_2\text{H}/\text{EPA}$ ) 354, 367.5, 385.5, 448 (sh), 465 (sh), 477 (sh), 495 (sh) nm;  $\lambda_{\text{max}}$  ( $\text{CCl}_3\text{CO}_2\text{H}/\text{EPA}$ ) 345.5, 371, 428 (sh), 448, 477 nm.

**Measurement of the Infrared Absorption Spectra in  $\text{CFCl}_3$ – $\text{CF}_2\text{BrCF}_2\text{Br}$ – $\text{CHCl}_3$  at  $-155^\circ\text{C}$ .** The measurements of IR spectra of **1** [ $^{16}\text{O}$ ], **1** [ $^{18}\text{O}$ ], and tropone at low temperature were performed by using an instrument of Ikawa et al.<sup>40</sup> A mixture of  $\text{CFCl}_3$ – $\text{CF}_2\text{BrCF}_2\text{Br}$ – $\text{CHCl}_3$  (25:25:4) formed a clear glass at  $-155^\circ\text{C}$ .

**Thermal Generation of 1 from 2 and Its Trapping with Maleic Anhydride.** A solution of 100 mg of **2** (0.64 mmol) and 630 mg of maleic anhydride (6.4 mmol) in 15 mL of benzene was heated at  $220^\circ\text{C}$  for 55 h in a glass ampule. The GLC analysis (10% Silicon SE30, 1 m,  $100$ – $250^\circ\text{C}$ ) of the mixture showed the 85% consumption of **2** and the formation of a single product (65% by GLC). After removal of the solvent, the residue was chromatographed on silica gel eluted with  $\text{AcOEt}/\text{hexane}$  (1:99) to afford 15 mg of **2** (15% recovery). Further elution with  $\text{AcOEt}/\text{hexane}$  (1:9) afforded 70 mg of **12** (52%) as colorless crystals: mp  $227.5$ – $228.5^\circ\text{C}$ ;  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.78 (dd,  $J = 9.8$  and  $1.7$  Hz, 1 H), 3.96 (dd,  $J = 9.8$  and  $2.2$  Hz, 1 H), 4.29 (ddd,  $J = 8.8, 1.7$ , and  $0.5$  Hz, 1 H), 4.47 (dd,  $J = 2.2$  and  $1.7$  Hz, 1 H), 5.87 (ddd,  $J = 10.5, 1.7$ , and  $0.5$  Hz, 1 H), 7.26–7.46 (m, 5 H);  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  42.71, 43.42, 48.15, 59.74, 127.51, 128.83, 128.95, 129.03, 129.36, 131.51, 138.72, 151.27, 171.36, 172.34, 193.30; IR (KBr) 1854, 1778,  $1664 \text{ cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (EtOH) 228 ( $\epsilon$  8400), 260 (830, sh), 340 nm (160); MS  $m/z$  254 ( $\text{M}^+$ , 76), 226 (51), 181 (100); HRMS calcd for  $\text{C}_{15}\text{H}_{10}\text{O}_4$  254.0579, found 254.0588.

**Thermal Generation of 1 from 2 and Its Trapping with Ethyl Vinyl Ether.** A solution of 40 mg of **2** (0.26 mmol) and 1 mL of ethyl vinyl ether (10.5 mmol) in 5 mL of benzene was heated at  $220^\circ\text{C}$  for 60 h in a glass ampule. The GLC analysis (5% PEG20M, 1 m,  $120$ – $220^\circ\text{C}$ ) of the mixture showed the almost complete consumption of **2** and the formation of three volatile products **13**, **14**, and **15** in GLC yields of 10%, 7%, and 15%, respectively. After removal of the volatile material, the residue was chromatographed on silica gel eluted with benzene/hexane (1:1) to afford **15**, which was further purified by preparative GLC (3.2 mg, 6%). Further elution with ether/hexane (3:7) produced a mixture of **13** and **14**, which were further purified by preparative GLC to give 3.0 mg of **12** (5%) and 2.9 mg of **13** (5%). **13**:  $^1\text{H}$  NMR  $\delta$  1.11 (t,  $J = 6.8$  Hz, 3 H), 1.95 (ddd,  $J = 14.6, 5.8$ , and  $2.4$  Hz, 1H), 2.53 (ddd,  $J = 14.6, 8.8$ , and  $1.5$  Hz, 1 H), 3.45 (dq,  $J = 9.3$  and  $6.8$  Hz, 1 H), 3.56 (dq,  $J = 9.3$  and  $6.8$  Hz, 1 H), 3.95 (ddd,  $J = 5.8, 2.0$ , and  $1.5$  Hz, 1 H), 3.96 (dd,  $J = 9.3$  and  $2.0$  Hz, 1H), 4.16 (ddd,  $J = 11.2, 2.4$ , and  $2.0$  Hz, 1 H), 5.76 (dd,  $J = 11.2$  and  $2.0$  Hz,

(40) Hashimoto, S.; Ohba, T.; Ikawa, S.-I. *Chem. Phys.* **1989**, *138*, 63.



1 H), 7.14 (dd,  $J = 11.2$  and  $9.3$  Hz, 1 H), 7.16–7.28 (m, 4 H); IR (film) 1670, 1588, 1488  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (EtOH) 234 ( $\epsilon$  7700), 345 nm (180); MS  $m/z$  228 ( $M^+$ , 53), 128 (100); HRMS calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_2$  228.1150, found 228.1137. **14**:  $^1\text{H}$  NMR  $\delta$  1.23 (t,  $J = 6.8$  Hz, 3 H), 1.94 (dd,  $J = 14.6$  and  $4.4$  Hz, 1 H), 2.59 (ddd,  $J = 14.6$ ,  $8.8$  and  $6.8$  Hz, 1 H), 3.55 (dq,  $J = 9.3$  and  $6.8$  Hz, 1 H), 3.64 (dq,  $J = 9.3$  and  $6.8$  Hz, 1 H), 3.89 (dd,  $J = 6.8$  and  $1.9$  Hz, 1 H), 3.96 (dd,  $J = 8.8$  and  $4.4$  Hz, 1 H), 4.16 (dd,  $J = 8.8$  and  $4.4$  Hz, 1 H), 5.92 (dd,  $J = 11.2$  and  $1.9$  Hz, 1 H), 7.07 (dd,  $J = 11.2$  and  $8.8$  Hz, 1 H), 7.14–7.27 (m, 4 H); IR (film) 1668, 1586, 1488  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (EtOH) 230 ( $\epsilon$  7500), 335 nm (190); MS  $m/z$  228 ( $M^+$ , 47), 128 (100); HRMS calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_2$  228.1150, found 228.1151. **15**:  $^1\text{H}$  NMR  $\delta$  1.27 (t,  $J = 6.8$  Hz, 3H), 3.10 (dd,  $J = 13.2$  and  $6.8$  Hz, 1 H), 3.11 (dd,  $J = 16.6$  and  $2.9$  Hz, 1 H), 3.14 (dq,  $J = 13.2$  and  $6.8$  Hz, 1 H), 3.43 (dd,  $J = 16.6$  and  $7.3$  Hz, 1 H), 3.64 (dq,  $J = 9.3$  and  $6.8$  Hz, 1 H), 3.93 (dq,  $J = 9.3$  and  $6.8$  Hz, 1 H), 5.67 (dd,  $J = 7.3$  and  $2.9$  Hz, 1 H), 5.81 (dt,  $J = 9.8$  and  $6.8$  Hz, 1 H), 6.11 (d,  $J = 9.8$  Hz, 1 H), 7.16–7.26 (m, 4 H); IR (film) 1634, 1604, 1564, 1490  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (EtOH) 230 ( $\epsilon$  9000, sh), 303 nm (8300); MS  $m/z$  228 ( $M^+$ , 93), 199 (50), 128 (100); HRMS calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_2$  228.1150, found 228.1151.

**Photolysis of 2 in Methanol at Ambient Temperature.** A solution of 156 mg of **2** (1.0 mmol) in 150 mL of methanol was placed in a Pyrex vessel, bubbled with argon for 30 min at  $0^\circ\text{C}$ , and irradiated with a high-pressure Hg lamp at  $10^\circ\text{C}$  for 20 min. The photolyzate was allowed to stand at room temperature for 2 days in the dark, concentrated, and subjected to chromatography on silica gel eluted with ether/hexane (1:9) to give 46 mg of **23** (34%) and 9 mg of **21** (7%). Further elution with ether/hexane (2:8) gave 38 mg of **2** and 6 mg of methyl ether which resulted from the conjugate addition of methanol to the enone moiety of **2** in the dark (combined recovery 28%). Further elution with ether gave a mixture of **7**, **8**, **9**, and **22**, which was subjected to preparative HPLC ( $\mu$ -Porasil, ether/hexane 1:2) to afford 5 mg of **7** (4.4%), 5 mg of **8** (4.4%), 4 mg of **9** (3.6%), and 12 mg of **22** (8.9%). **21**:  $^1\text{H}$  NMR  $\delta$  3.43 (s, 2 H), 3.53 (s, 2 H), 3.67 (s, 3 H), 6.69 (s, 1 H), 7.11–7.38 (m, 4 H); IR (film) 1738, 1202, 1170  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (EtOH) 257 ( $\epsilon$  12 800), 281 (1300), 288 nm (500, sh); MS  $m/z$  188 ( $M^+$ , 29), 129 (100), 128 (81). Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$ : C, 76.57; H, 6.43. Found: C, 76.40; H, 6.44. **21**:  $^1\text{H}$  NMR  $\delta$  2.14 (d,  $J = 17.5$  Hz, 1 H), 2.37 (dd,  $J = 17.5$  and  $3.5$  Hz, 1 H), 3.31 (s, 3 H), 3.74 (dd,  $J = 3.5$  and  $1.5$  Hz, 1 H), 3.79 (s, 3 H), 4.26 (t,  $J = 1.5$  Hz, 1 H), 7.18 (ddd,  $J = 7.8$ ,  $7.3$ , and  $1.0$  Hz, 1 H), 7.21 (ddd,  $J = 7.8$ ,  $7.3$ , and  $1.0$  Hz, 1 H), 7.30 (d,  $J = 7.3$  Hz, 1 H), 7.31 (d,  $J = 7.3$  Hz, 1 H); IR (film) 1752  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (EtOH) 258 ( $\epsilon$  720, sh), 266 (780), 275 (640), 290 (630, sh), 298 (810), 307 (820), 318 nm (480, sh); MS  $m/z$  188 ( $M^+$ , 26), 159 (24), 128 (100); HRMS calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$  188.0840, found 188.0843. **23**:  $^1\text{H}$  NMR  $\delta$  2.41 (dd,  $J = 16.1$  and  $9.3$  Hz, 1 H), 2.75 (dd,  $J = 16.1$  and  $6.9$  Hz, 1 H), 3.76 (s, 3 H), 3.87 (ddt,  $J = 9.3$ ,  $6.9$ , and  $1.5$  Hz, 1 H), 6.54 (dd,  $J = 5.4$  and  $1.5$  Hz, 1 H), 6.83 (dd,  $J = 5.4$  and  $1.5$  Hz, 1 H), 7.19 (t,  $J = 7.3$  Hz, 1 H), 7.28 (t,  $J = 7.3$  Hz, 1 H), 7.36 (d,  $J = 7.3$  Hz, 1 H), 7.39 (d,  $J = 7.3$  Hz, 1 H); IR (film) 1738, 1236  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (EtOH) 252 ( $\epsilon$  6000), 282 (950, sh), 288

nm (700, sh); MS  $m/z$  188 ( $M^+$ , 48), 129 (100), 128 (78). Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$ : C, 76.57; H, 6.43. Found: C, 76.11; H, 6.27.

**Photolysis of 2 in Methanol. Sensitizing and Quenching Experiments.** A degassed methanolic solution of **2** (3 mL,  $2.0 \times 10^{-2}$  M) in a quartz cell was irradiated with a 500 W high-pressure Hg lamp through a solution filter of  $\text{K}_2\text{CrO}_4$  aq (313 nm light) for 30 min. The photolyzate was allowed to stand at room temperature for 2 d and analyzed by GLC (OV-1 capillary column, 30 m,  $120^\circ\text{C}$ ) and HPLC ( $\mu$ -Porasil, ether/hexane 1:2). The conversion of **2** and the formation of the methanol adducts were monitored by GLC, while the yields of the dimers of **1** were determined by HPLC. Dimethyl phthalate was used as a common internal standard for these analyses. To the methanolic solution of **2** (3 mL) was added 7 mg of xanthone ( $1.2 \times 10^{-2}$  M, >95% of 313 nm light was absorbed,  $E_T = 74$  kcal/mol<sup>26</sup>) for the sensitizing experiment while 0.3 mL of freshly distilled 1,3-pentadiene (a mixture of cis and trans isomers, 1.0 M,  $E_T = 57$ –59 kcal/mol<sup>26</sup>) was added for the quenching experiment. The conversions of **2** in the direct photolysis and in the sensitizing and quenching experiments were 35%, 42%, and 13%, respectively. The formation of product mixture with nearly the same composition was observed in all the experiments.

**Photolysis of 2 in  $\text{CHCl}_3$  at  $-10^\circ\text{C}$ . Detection of 3,4-Benzotricyclo-[3.2.0.0<sup>2,7</sup>]hept-3-en-6-one (19).** A solution of 10 mg of **2** in 0.6 mL of  $\text{CHCl}_3$  in a Pyrex test tube (10 mm i.d.) was bubbled with  $\text{N}_2$  for 10 min at  $0^\circ\text{C}$  and irradiated with a high-pressure Hg lamp through a Corning 7-60 filter (365 nm light) for 90 min at  $-10^\circ\text{C}$ . The IR spectrum of the photolyzate showed development of an absorption band at 1746  $\text{cm}^{-1}$ , which was assigned to **19**, together with a weak band at 2116  $\text{cm}^{-1}$ . When the resultant solution was allowed to stand at room temperature in the dark, the intensity of the band at 2116  $\text{cm}^{-1}$  grew at the expense of the band at 1746  $\text{cm}^{-1}$ .

A solution of 5 mg of **2** in 0.7 mL of  $\text{CDCl}_3$  in an NMR tube was irradiated with a high-pressure Hg lamp through a Corning 7-60 filter (365 nm light) for 90 min at  $-10^\circ\text{C}$ . The 500 MHz  $^1\text{H}$  NMR spectrum of the photolyzate showed the formation of a single major product (50% yield by NMR) along with the complete consumption of **2**. The observed spectrum was consistent with the structure of **19**:  $^1\text{H}$  NMR  $\delta$  3.11 (ddd,  $J = 5.9$ ,  $3.9$ , and  $3.4$  Hz, 1 H), 3.33 (ddd,  $J = 3.4$ ,  $2.4$ , and  $1$  Hz, 1 H), 4.05 (ddd,  $J = 3.4$ ,  $2.4$ , and  $1$  Hz, 1 H), 4.10 (ddd,  $J = 4.4$ ,  $3.9$ , and  $2.4$  Hz, 1 H), 7.10–7.17 (m, 3 H), 7.35 (br d,  $J = 7.3$  Hz, 1 H).

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